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Reactive blending of polyamide 6,6 and Vectra A

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Abstract

In this paper, blends of Nylon 6,6 with the liquid crystal polymer Vectra A950 are considered; specifically we focused our attention on Nylon 6,6 modifications by interchange reactions that can occur in the melt, as a function of mixing conditions and blend compositions. Two matrix samples have been used, characterised by a slightly different relative amount of amine and carboxylic end groups, being the latter predominant in both cases. The dried polymers Nylon 6,6/Vectra, combined in weight ratios between 95/5 and 50/50, were subjected to reactive blending with different methods (single-screw extruder, Brabender, pyrex reactor). Pure Nylon samples have been also investigated as reference materials. The soluble Nylon 6,6-rich fraction of each blend was separated from the insoluble Vectra-rich one and used for molecular and spectroscopic characterisations. Thermal and morphological analyses, as well as testing of tensile properties, were carried out on the blends. Evidences of the occurrence of interchange reactions are given and the most probable ones are suggested. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Interchange reactions; Nylon 6,6

1. Introduction

Blending of thermotropic liquid crystal polymers (LCPs) with conventional thermoplastics (TPs) has attracted much attention over the last two decades, since it represents an interesting perspective for the attainment of in situ composites, where fibrous reinforcement forms directly during processing, as a consequence of the easy orientability and the long relaxation times of LCPs [1,2]. Several data have been reported in papers and comprehensive reviews [1–8]; some general concepts emerge from them, concerning the suitable processing techniques to achieve controlled orientation of LCPs in the molten state, together with their freezing in the proper morphology, and the role of compatibility and interfacial adhesion.

Since polymer pairs are generally immiscible and incompatible, their blending can result in products with mechanical properties poorer than the average of the two components; in the case of LCP/TP composites this aspect could be enhanced by the phase heterogeneity of the melt. Reinforcing effects arise from compatibility between matrix and dispersed phase, as it determines interfacial adhesion between immiscible homophases; moreover, a reduction of interfacial tension between blend components decreases the domain size of the dispersed phase. In situ formed copolymeric products by interchange reactions in the melt between blend constituents is expected to improve compatibility and adhesion extent, thus enhancing mechanical properties. Indeed, the occurrence of interchange reactions during processing has been considered the origin of the partial miscibility observed in some mixtures of traditional components [9–11].

Although significant work has been carried out on blends of LCPs with polyesters, mainly PET and PC [12–17], few information can be found on polyamide/LCP systems, and in particular on Nylon 6,6 based blends. Lekakou et al. [18] investigated how to improve mechanical properties of injection moulded specimens based on Nylon 6,6 varying processing conditions and blend composition. The blend with 25 vol% of Vectra, injection moulded under the optimum processing conditions found for pure Vectra, displays the best reinforcing properties. Rheology, morphology and properties of Vectra A/Nylon 6,6 composite fibres have been very recently investigated by Wang et al. [19]. The viscosity ratio of LCP and matrix and the mixture composition appear to be critical factors in determining the blend morphology; mechanical properties of the composite fibres are below the rule of mixtures if the LCP content is low, above the rule of mixtures for high LCP concentrations.

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Table 1
Molecular characteristics of Nylon 6,6 samples

Nylon 6,6	COOH end group (meq kg^{-1})	NH$_2$ end group (meq kg^{-1})	COOH/NH$_2$	η_{inh} (dl g^{-1})
Nylon I	30.0	15.0	2	1.70
Nylon II	51.8	19.5	2.6	1.56

In this work, Nylon 6,6/Vectra A blends have been prepared and investigated; in particular we focused our attention on Nylon 6,6 modifications due to interchange reactions that can occur in the melt, as a function of mixing conditions and blend compositions, and can improve the compatibility of the blend. Two matrix samples have been used, characterised by a slight difference in the relative amount of amine and carboxylic terminal groups, being the latter predominant in both cases.

2. Experimental

2.1. Materials

The matrix polymers used in this work were two different Nylon 6,6, identified as Nylon I and Nylon II. Their molecular characteristics are shown in Table 1; for both samples the carboxylic function is the predominant end group. The LCP was Vectra A950, produced by Ticona, a wholly aromatic copolyester made of 27 mol% of 6-hydroxy-2-naphtoic acid (HNA) and 73 mol% of *p*-hydroxy-benzoic acid (HBA); it shows a glass transition temperature at about 105°C and a nematic melt at 278°C. As the majority of thermotropic LCPs of commercial significance, Vectra A is prepared by an ester exchange reaction (melt acidolysis reaction) between acetoxyaryl groups and carboxylic acid groups with the elimination of acetic acid, at temperatures above the melting point of the resultant polymer [20,21]; therefore it bears acetoxyaryl and carboxylic end groups. Vectra and Nylon 6,6 were dried under vacuum at 110 and 90°C, respectively, for at least 24 h before blending.

The dried polymers Nylon 6,6/Vectra, combined in weight ratios 95/5, 90/10, 80/20 and 50/50, were subjected to melt blending with different methods, as indicated in Table 2. Blends of Nylon I/Vectra (95/5, 90/10 and 80/20) and Nylon II/Vectra (90/10) were fed to a Gi.Mac. single-screw extruder (*L*/*D* ratio = 22) equipped with a Ross ISG static mixer, containing a sequence of 12 mixing elements. The extruder zones were set at 290°C; the temperature of the mixing section was 305°C and the die exit temperature 300°C. The screw speed was 50 rpm. Blends of Nylon II and Vectra (composition 90/10 and 80/20) were also prepared by melt mixing under Argon in a 30 ml mixing room of a Brabender Plastograph at 30 rpm and 290°C for 10 and 20 min. Moreover, melt blending of Nylon I or Nylon II and Vectra (50/50) was carried out in a cylindrical pyrex reactor, equipped with a mechanical stirrer and gas-inlet and -outlet tubes. The mixture components were placed into the reactor maintained in a pre-heated metal bath and allowed to blend at 300°C for 20 or 30 min under stirring; a dry nitrogen flux was injected through the system.

Table 2
Composition, mixing conditions of Nylon/LCP blends and solution viscosity of soluble fractions

Matrix	Nylon 6,6/Vectra composition (w/w)	Mixing technique	*T* (°C)	*t* (min)	η_{inh} (dl g^{-1})
Nylon I	100/0	Pellets			1.70
	100/0	Extruder	300[a]	–	1.43
	95/5	Extruder	300[a]	–	–
	90/10	Extruder	300[a]	–	–
	80/20	Extruder	300[a]	–	1.06
	100/0	Glass reactor	300	30	1.62
	50/50	Glass reactor	300	20	–
	50/50	Glass reactor	300	30	0.54
Nylon II	100/0	Pellets			1.56
	100/0	Extruder	300[a]	–	1.32
	90/10	Extruder	300[a]	–	1.01
	100/0	Brabender	290	20	1.31
	90/10	Brabender	290	20	–
	80/20	Brabender	290	20	1.21
	80/20	Brabender	290	10	1.31
	100/0	Glass reactor	300	30	1.59
	50/50	Glass reactor	300	30	0.43

[a] Temperature at the die exit.

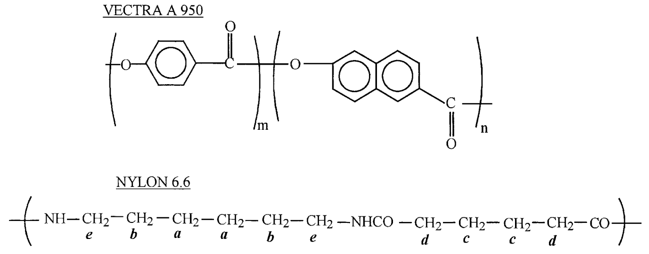
High mixing temperatures were adopted for all blending methods in order to increase the kinetics of interchange reactions. Pure Nylon samples, thermally treated under the same conditions as blends, have been also investigated as reference materials.

2.2. Characterisation techniques

Molecular (viscosity of dilute solutions) and structural (FT-IR, UV–VIS and ^{1}H-NMR) characterisation was performed on the formic acid soluble fractions of the blends. Thermal (DSC and TGA) and morphological (SEM) analyses were carried out on blends as prepared.

A suitable amount of all the blends was maintained in formic acid (concentration 2%, w/v) at room temperature for 24 h under stirring. The Vectra-rich fraction, insoluble in formic acid, was separated from the soluble Nylon 6,6-rich one using an ultracentrifuge Beckman, model J2-21, at 14,000 rpm for at least 12 h. The soluble fraction was precipitated in methanol, filtered, dried under vacuum and then used for molecular and spectroscopic characterisations.

Viscosity measurements of dilute solutions were made at 25°C with an Ubbelhode viscometer, using sulphuric acid 96% as solvent at a concentration of 0.5 g dl^{-1}. Infrared analysis was carried out on a Bruker IFS 28 instrument between 400 and 4000 cm^{-1}: soluble samples were analysed as thin films obtained by evaporation of formic acid from 1% (w/v) solutions; the insoluble fractions were investigated



Scheme 1.

by the KBr method. UV spectra of the soluble fractions were recorded between 220 and 400 nm on a Perkin–Elmer UV–VIS Lambda 2 spectrometer; 1% (w/v) HCOOH solutions were generally used. ^{1}H-NMR analysis on the soluble fractions was carried out on a Varian–Gemini spectrometer model 2000, using D_2SO_4 as solvent and TMS as internal standard.

Thermal transitions were studied through a differential scanning calorimeter Mettler TA 3000 (measuring cell DSC 30), equipped with a software package Graphware TA72. The samples were heated from 0 up to 320°C at a scanning rate of 20°C/min and kept at this temperature for 3 min; after cooling to 0°C at −20°C/min a second heating run was performed up to 320°C at the same scanning rate. Thermal stability was tested on blends and neat Nylon samples with a Perkin–Elmer TGS 2 analyser (heating rate 10°C/min under nitrogen). The blend morphology was studied with a scanning electron microscope (SEM) Leica Stereoscan 440 at 20 kV accelerating voltage; the analyses were carried out on samples fractured in liquid nitrogen and coated with gold in a sputtering coating unit, mod. Agar Aid PS 3.

Specimens for testing mechanical properties were prepared from sample sheets obtained by fast cooling after melting at 290°C and pressing at 10 MPa the dried blends and neat Nylon 6,6 materials in a Carver Laboratory press model C. The sheets were cut in rectangular specimens 80 mm × 10 mm × 1 mm sized and tested for tensile properties on an Instron 5565 machine equipped with a software package Merlin Series IX.

3. Results and discussions

Viscosity measurements, carried out on the soluble fractions of the blends and on neat Nylon samples dissolved in HCOOH and precipitated with methanol after thermal treatments, exhibit a lower η_{inh} than the original materials, as shown in Table 2. A certain decrease of η_{inh} seems to be due to the thermal treatment; indeed, the values of treated Nylons are generally lower than those of the corresponding pellets. However, the viscosity drop is enhanced whenever the amount of Vectra in the blend and/or the mixing time are increased. This effect might arise from the presence of short chains of LCP bound to Nylon molecules by interchange reactions, that should cause a stiffening of Nylon chains; however, the strong decrease of η_{inh}, revealed by the 50/50 blends, suggests the occurrence of chemical reactions able to reduce the length of Nylon chains.

The presence of Vectra segments bound to Nylon molecules is confirmed by spectroscopic analyses (FT-IR, ^{1}H-NMR, UV). Actually, by comparing IR spectra of neat Nylons I and II with those of the soluble fractions of the blends, some differences emerge, that can be due to the contribution of small segments of bound Vectra. A little shoulder around 1730 cm^{-1} appears in the spectrum of the soluble fraction of the blends, that is not present in the spectrum of neat Nylons and could be ascribed to the presence of bound Vectra segments, since it is characteristic of the Vectra carbonyl. Unfortunately, this shoulder at 1730 cm^{-1} is hardly observable in the FT-IR profile of blends bearing low percentages of Vectra; probably, in these mixtures, the amount of Vectra reacted with the matrix is too low to be revealed by the analysis.

One of the most appropriate methods to investigate the chemical structure of reactive blends is ^{1}H-NMR spectroscopy. Application of this technique for studying LCP based blends is reported in some papers [15,20,21] to demonstrate the occurrence of interchange reactions. For the HCOOH soluble fractions of the melt blended Nylon 6,6/Vectra mixtures the appearance of signals that can be assigned to aromatic protons (see Scheme 1) confirms that a certain amount of LCP is chemically bound to Nylon. Spectrum a of Fig. 1 refers to neat Nylon I, thermally treated into the glass reactor; the typical peaks of methylene protons are clearly evident between 0.5 and 3.0 ppm. Profiles 1b and 1c relate to the spectra of the soluble fractions of the 50/50 Nylon I/Vectra and Nylon II/Vectra blends, respectively. A series of small signals appear between 6.4 and 8.4 ppm, in the field of typical aromatic protons, better evident in the expanded Fig. 1d. Small-scale signals refer to naphthalene unit protons, more intense signals to benzene ring protons. Because of the aromatic nature of Vectra protons, the amount of reacted LCP revealed by the comparison between the areas of aliphatic and aromatic signals can be underestimated, then the compatibilisation reaction probably occurs to a higher extent. In order to verify the occurrence of a chemical binding between Nylon and Vectra sequences, ^{1}H-NMR analysis was also carried out on the HCOOH soluble fraction of a mechanical mixture of the right amount of the two blend components prepared at room temperature. The result, given in Fig. 1e, is identical to spectrum a of the same figure and eliminates any doubt about a partial solubility of Vectra molecules in a solvent mixture made of formic acid and polyamide.

UV analysis on the soluble fraction of the blends reveal a broad absorption with a maximum ranging around 250 nm, not displayed by neat Nylon; in Fig. 2 spectra of the mixtures 80/20 Nylon I/Vectra (curve c) and 90/10 Nylon I or Nylon II/Vectra (curves d and e) prepared in the extruder are compared with that of extruded Nylon I (curve f).

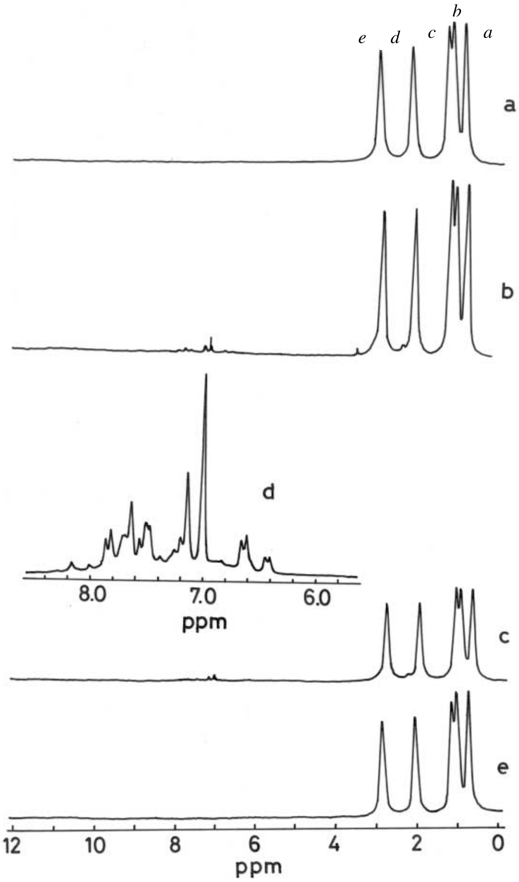


Fig. 1. ^{1}H-NMR spectra: (a) neat Nylon I from the glass reactor; (b) soluble fraction of the Nylon I/Vectra 50/50 blend (glass reactor); (c) soluble fraction of the Nylon II/Vectra 50/50 blend (glass reactor); (d) expansion of the zone between 6.4 and 8.4 ppm; (e) soluble fraction of a room temperature mechanical mixture Nylon II/Vectra 50/50 (solvent: D_2SO_4; internal standard: TMS).

Curve g refers to the original pellets of Nylon I. A higher percentage of LCP in the blend causes a higher absorption; at fixed composition the absorption is independent of the matrix. Mixtures based on Nylon II prepared in Brabender exhibit different absorption depending on both mixing time and blend composition; longer times, as well as higher LCP contents, result in increased absorption. For Nylon II based blend with 50% LCP and mixing times of 20 and 30 min absorption is so intense that more diluted HCOOH solutions (0.25%, w/v) had to be used to obtain spectra a and b of Fig. 2. These results confirm the occurrence of reactive blending between Vectra and Nylon, favoured by residence time and LCP concentration.

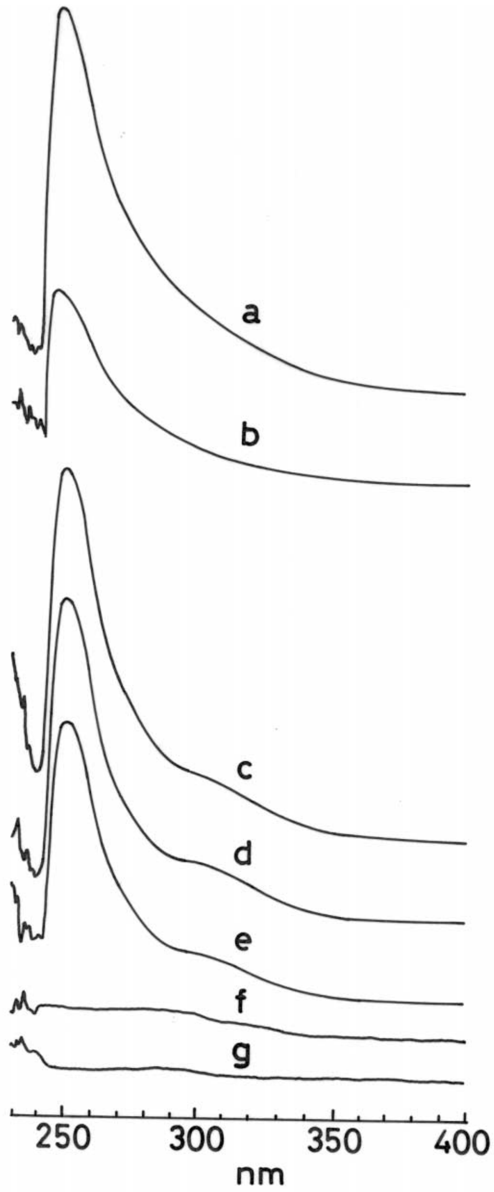


Fig. 2. UV–VIS spectra: (a) soluble fraction of the Nylon II/Vectra 50/50 blend (glass reactor: 30 min; concentration 0.25% w/v); (b) soluble fraction of the Nylon II/Vectra 50/50 blend (glass reactor: 20 min; concentration 0.25%, w/v); (c) soluble fraction of the extruded Nylon I/Vectra 80/20 blend; (d) soluble fraction of the extruded Nylon I/Vectra 90/10 blend; (e) soluble fraction of the extruded Nylon II/Vectra 90/10 blend; (f) neat Nylon I from the extruder; (g) original Nylon I pellets.

Table 3 shows the results of DSC analysis on blends based on Nylon I and Nylon II; data of ΔH are normalised to the real content of Nylon in the blends. For both Nylons the lowest crystallisation temperatures are shown by the original pellets; memory effects after thermomechanical treatments during mixing cause this result. For extruded samples small amounts of Vectra in the mixtures (5–10%) act as nucleation agents, slightly increasing the crystallisation temperature T_c of the matrix. This effect is mentioned in the literature for different matrix/LCP systems [22–26]; moreover, the mixing procedure affects the crystallisation kinetics, as shown by the Nylon II based samples prepared in Brabender, as a consequence of a stronger thermomechanical orienting effect arising in Brabender from higher mixing times at a lower processing temperature. High Vectra contents disturb the crystallisation of Nylons, as shown by the reduced values of T_m and T_c of the 50/50

Table 3
DSC analysis on Nylon I and II based blends and some soluble fractions

Nylon /Vectra blends (w/w)	Mixing technique	First heating		Cooling		Second heating	
		T_m (°C)	ΔH_m (J g_{Ny}^{-1})	T_c (°C)	ΔH_c (J g_{Ny}^{-1})	T_m (°C)	ΔH_m (J g_{Ny}^{-1})
Nylon I pellets	–	262.9	63.1	207.9	53.8	258.6	60.9
100/0	Extruder	263.3	70.2	223.3	59.1	259.5	67.5
95/5	Extruder	263.0	65.9	227.6	62.7	260.5	75.5
90/10	Extruder	264.5	59.8	228.6	63.1	260.9	74.3
80/20	Extruder	262.1	66.1	228.4	68.1	260.0	77.3
100/0	Glass reactor	260.3	67.0	222.0	59.3	258.2	68.5
50/50	Glass reactor	248.7	70.1	216.8	54.7	244.1	67.2
Nylon II pellets	–	266.3	62.3	200.4	55.3	263.3	56.1
100/0	Extruder	262.7	69.7	226.6	61.3	261.3	69.8
90/10	Extruder	262.8	73.2	230.8	64.9	261.5	75.5
100/0	Brabender (20 min)	268.1	81.3	230.6	63.9	260.7	77.8
90/10	Brabender (20 min)	264.8	68.8	231.8	64.1	264.7	79.7
80/20	Brabender (10 min)	264.9	72.6	228.4	64.2	261.6	77.9
80/20	Brabender (20 min)	266.2	77.1	229.3	61.1	261.8	76.9
100/0	Glass reactor	263.4	59.1	222.2	59.8	261.1	67.2
50/50	Glass reactor	251.2	65.1	210.2	60.6	247.3	69.5
80/20 (soluble fraction)	Brabender (10 min)	264.3	95.2	232.3	63.5	261.8	76.6
80/20 (soluble fraction)	Brabender (20 min)	266.0	94.1	233.5	61.5	260.6	73.4
50/50 (soluble fraction)	Glass reactor	260.9	95.2	227.8	64.0	256.4	76.5

blends prepared in the glass reactor; a slower kinetics of crystallisation generates smaller and/or less perfect low-melting crystals. However, upon removing the insoluble Vectra-rich fraction by extraction with HCOOH, melting and crystallisation temperatures come back to the expected level (see data on the soluble fraction of the 50/50 blend). ΔH_m of the first heating on the soluble fractions of Nylon II based samples are very high, since crystals formed by precipitation from HCOOH solutions with methanol have a higher degree of perfection than the ones build up by cooling the molten blends. The little increase of T_c shown by the soluble fractions of the blends can be ascribed to a memory effect and/or to a nucleation action played by short segments of bound Vectra.

TGA analysis on Nylon I, Nylon II and their extruded blends (Table 4) indicates a small decrease (of about 10°C) of the onset temperature of degradation with both the thermal treatment and the addition of 10% of Vectra. In other words, even if the degradation temperature of Vectra is much higher (about 50°C) than that of neat Nylons, the presence of 10% of Vectra negatively affects the thermal stability of the polyamides. Given that this effect is limited to few percents, it should be substantially ineffective on the blend properties.

SEM analysis of the Nylon I/Vectra 95/5, 90/10, 80/20 and Nylon II/Vectra 90/10 mixtures prepared in the extruder (Figs. 3a–c and 4a) clearly shows a biphasic morphology typical of highly immiscible blends and a quite good dispersion of Vectra into the matrix. The shape of the Vectra domains is spherical (diameter between 1 and 6 μm); a certain degree of interface adhesion is suggested by the presence of strained material on the surface of the domains and by the presence of fibrillar microdomains of Vectra on the surface of the empty holes arising from the pulling off of the dispersed phase (Fig. 4b). However compatibilisation is still limited and unable to give a very good adhesion between the two polymers. This morphology does not change after compression moulding carried out to prepare specimens for mechanical testing. Mixing in Brabender rather than in the extruder increases the residence time and results in a finer dispersion of the minor component. Moreover, the dispersed domains exhibit a certain degree of orientation, as a result of the stronger thermomechanical effect of mixing. Fig. 5 shows three micrographs of samples obtained in Brabender from Nylon II and 10% of Vectra with a blending time of 20 min (micrograph a) and 20% of Vectra with mixing times of 10 and 20 min (micrograph b and c, respectively). Besides the blend composition, that obviously affects the sample morphology, the longer mixing time originates a larger number of small-sized domains and then a better dispersion of Vectra. A finer size of the

Table 4
TGA on extruded blends and pure components

Matrix	Nylon 6,6/Vectra composition (w/w)	Onset degradation temperature (°C)
Nylon I	100/0 Pellets	447.2
	100/0	437.7
	90/10	428.8
Nylon II	100/0 Pellets	439.5
	100/0	430.6
	90/10	423.4
Vectra	0/100 Pellets	505.0

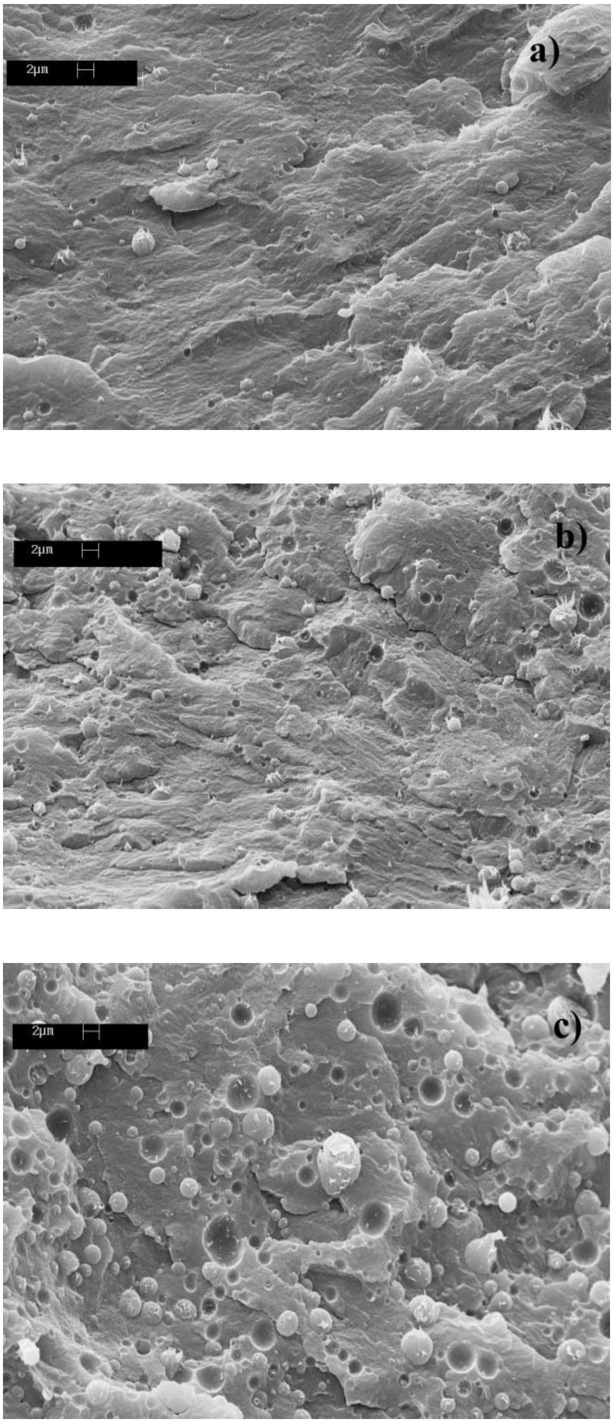


Fig. 3. SEM micrographs of the fracture surface of extruded blends of Nylon I and Vectra: (a) composition 95/5; (b) composition 90/10; (c) composition 80/20.

dispersed phase on increasing melt-mixing time increases the contact surface between the two phases and should result in a higher possibility to form mixed copolymers. Therefore, the effect of mixture composition and mixing time on the extent of reactive blending, revealed by spectroscopic analyses, is qualitatively confirmed by morphology.

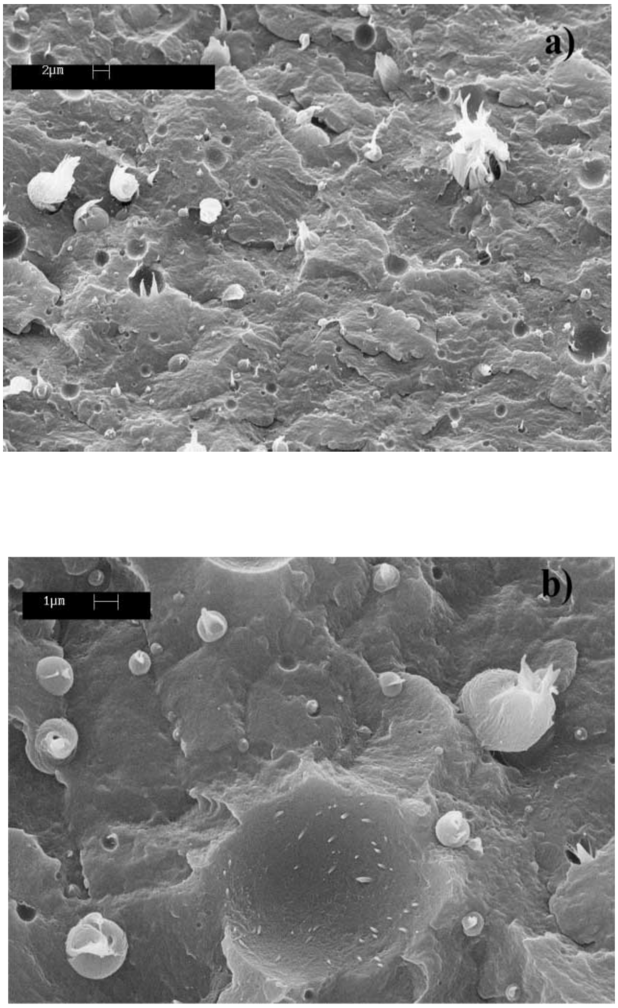


Fig. 4. SEM micrographs of the fracture surface of extruded blends of Nylon and Vectra: (a) Nylon II/Vectra 90/10; (b) a higher magnification for the Nylon II/Vectra 90/10 mixture.

About mechanical properties, the results obtained on extruded blends based on Nylon I (Table 5) show a modest increase of Young's modulus with Vectra content. The values of tensile strength and elongation at break decrease from neat Nylon to blends, since the material becomes more brittle when the percentage of Vectra increases. Inadequate interactions between spherical domains of Vectra and Nylon make the polyamide matrix weaker and unable to transfer mechanical stresses to LCP. Then, interface between components is the starting point of breaking and collapse of the matrix. The poor effect of LCP on mechanical properties of the blends can be justified on the basis of the specimen preparation technique, unable to induce orientation of the dispersed phase; it is commonly observed that processing operations in shear flow give rise to materials with tensile modulus similar to that of the flexible matrix [2]. Moreover, mixing conditions, in terms of temperature and residence time, have been chosen with the aim of enhancing the slow rate of interchange reactions. Achievement of self-reinforcing TP/LCP blends depends on the ability to melt

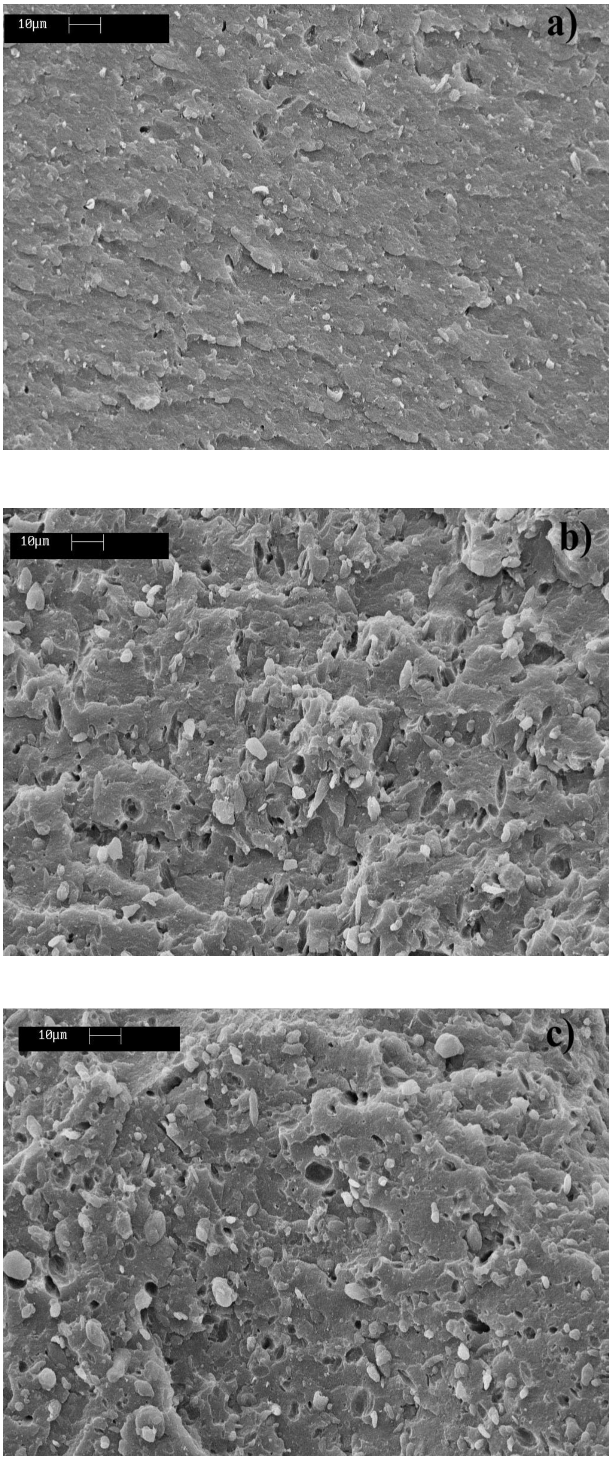


Fig. 5. SEM micrographs of the fracture surface of blends Nylon II/Vectra prepared in Brabender: (a) composition 90/10, mixing time 20 min; (b) composition 80/20, mixing time 10 min; (c) composition 80/20, mixing time 20 min.

Table 5
Mechanical properties on extruded blends

Matrix	Nylon 6,6/Vectra composition (w/w)	Young's modulus (MPa)	Tensile strenght (MPa)	Elongation at break (%)
Nylon I	100/0	1189	83	21
	95/5	1124	79	23
	90/10	1347	71	8
	80/20	1407	33	3

process the blend in such a way that LCP forms the reinforcing fibrillar phase. Interchange reactions between blend components can play an important role in influencing the fibrils' formation and the mechanical properties; nevertheless, to achieve optimal properties, a suitable processing technique able to control orientation of LCP is required. Factors affecting fibrils' formation, besides concentration of LCP relative to the matrix, type of deformation field and compatibility, are the viscosity ratio of LCP and matrix and the temperature dependence of the viscosity of the two components, i.e. the cooling characteristic of the LCP has to be matched with that of the TP matrix [1]. We have focused our attention on interface interactions arising from the production of in situ compatibilizing agents; however, full potential of LCP reinforcement cannot be exploited without optimising physical and rheological aspects.

4. Concluding remarks

The two Nylon samples, characterised by a slight different amount of end functional groups –COOH and –NH_2, show in mixture with Vectra a very similar behaviour. Then they offer little help to understand which Nylon end group is predominantly able to promote reactions with carboxylic, acetoxy or ester groups of Vectra. As far as the amine function is expected to be the most effective [27–29], the above results suggest that the difference in the relative concentration of the functional end groups of the examined samples is too low to induce evident effects.

Chemical reactions that may be involved by blending at high temperature Nylon and Vectra are summarised in Table 6; reactions between functional groups of Nylon leading to chain extension as well as hydrolytic degradation of the matrix have been omitted. The extent of each reaction, the reaction site and the final location of the reacted products are complex to define, but fundamental to design optimised reactive compatibilisation conditions. Reactions 1a and 1b between functional end groups of the two blend components are usual polycondensation equilibria releasing small molecules (H_2O or CH_3COOH), that require suitable conditions and probably do not occur or occur insignificantly under typical melt blending. Earlier reports [30,31] on ester-amide interchange reactions 2a suggest that they do not take place to a detectable amount without the presence of a suitable acid catalyst. However, if reaction 1b occurs to some extent, favoured by the moderate molecular weight of Vectra and the high concentration of carboxyl end groups of Nylon, the released acetic acid might catalyse reaction 2a, that leads to a Nylon/Vectra copolymers with both blocks

Table 6
Chemical reactions that may be involved

1	Condensation reactions between amine and carboxyl or carboxyl and acetoxy groups (a) Ny–NH_2 + Vectra–COOH → Ny–NH–CO–Vectra + H_2O (b) Ny–COOH + Vectra–$OCOCH_3$ → Ny–COO–Vectra + CH_3COOH
2	Ester-amide interchange reactions (a) Ny–NHCO–Ny + Vectra–COO–Vectra → Ny–NHCO–Vectra + Ny–COO–Vectra
3	Acidolysis between carboxyl and ester or carboxyl and amide (a) Ny–COOH + Vectra–COO–Vectra → Ny–COO–Vectra + Vectra–COOH (b) Vectra–COOH + Ny–NHCO–Ny → Vectra–CONH–Ny + Ny–COOH
4	Aminolysis between amine and ester (a) Ny–NH_2 + Vectra–COO–Vectra → Ny–NHCO–Vectra + Vectra–OH
5	Alcoholysis between acetoxy and amide (a) Vectra–$OCOCH_3$ + Ny–CONH–Ny → Vectra–OCO–Ny + Ny–NHCO–CH_3

shorter than the original molecules. Interchange reactions 3a–5a probably occur to some extent; they are all favoured by the high concentration of ester groups (Vectra) and amide groups (Nylon). Moreover, reaction 3a involves the predominant –COOH end groups of Nylon molecules, reaction 4a the minor but more reactive –NH_2 functional groups of Nylon and reaction 5a the acetoxy terminal group of Vectra. Due to the heterogeneous nature of the molten blend all these reactions can take place only at the interface. Analytical techniques used in this work are unable to check the chemical structure of the insoluble Vectra-rich fractions. Results on the soluble Nylon-rich fractions suggest that the formation of mixed Nylon-Vectra copolymers is strictly related to the Vectra content of the blend and implies a reduction of Nylon chain length. This means that the more probable reactions occurring in the system are reactions 2a and 5a; under the mixing conditions used only a small amount of copolymeric species form because of the low reaction kinetics, physical and rheological aspects and/or heterogeneity of the system. In order to limit the effect of the above mentioned parameters a research is in progress to test the role of suitable catalysts, modified processing conditions and/or reactive additives able to improve the extent of reactions and the melt viscosity of the Polyamide matrix. The power of a Nylon 6,6 matrix with predominant –NH_2 end groups on its reactive blending with Vectra is also under study.

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